



Chemical equilibrium for the reactive system propionic acid + ethanol + ethyl propionate + water at 303.15 and 313.15 K



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ABSTRACT

Chemical equilibrium for the quaternary system propionic acid + ethanol + ethyl propionate + water was experimentally studied at 303.15 and 313.15 K and atmospheric pressure. The chemically equilibrium compositions were determined by gas chromatography and nuclear magnetic resonance analytical methods. It is shown that chemical equilibrium is reached both in homogeneous and heterogeneous area of composition of reactive mixture. The liquid – liquid equilibrium data for the surface of chemical equilibrium were obtained. The thermodynamic constants of chemical equilibrium at 303.15 and 313.15 K were determined.

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1. Introduction

Heterogeneous systems with chemical reactions are complex objects and their study gives new thermodynamic information, allows establishing new physical and chemical regularities. At the same time it is obvious not only fundamental, but also the practical importance of the problem of the splitting of liquid reaction mixtures. Such effect fundamentally changes the technological process of chemical synthesis. The object of our study is a quaternary reacting system with ethyl propionate synthesis reaction. Ethyl propionate is widely used in the food processing, flavor industry and biofuel production [1,2]. This ester is an important reagent in pharmaceutical industries, e.g. for the production of some anti-malarial drugs including pyrimethamine. Ethyl propionate has also other promising areas of application, for example, in the manufacture of lithium batteries [3]. The esterification is one of the main industrial methods of ester synthesis and the data on phase and chemical equilibria are necessary for the process design. Unfortunately despite a practical importance of ethyl propionate the data sets on equilibrium properties of system propionic

acid + ethanol + ethyl propionate + water are very limited.

The only experimental data related to the properties of propionic acid + ethanol + ethyl propionate + water system were presented by Macedo and Rasmussen in 1982 [4]. The vapor – liquid equilibrium (VLE) was determined for the ethyl propionate – propionic acid mixture at 358 and 368 K and pressure 134.28–573.05 mm Hg for 20 compositions of binary mixtures. The VLE data have been correlated by UNIFAC model.

The aim of our work is the study of CE in propionic acid + ethanol + ethyl propionate + water system at 303.15 and 313.15 K and atmospheric pressure in a wide range of compositions including homogeneous and heterogeneous areas of reactive solutions. Accordingly we determined the liquid – liquid equilibrium (LLE) for chemically equilibrium states, i.e. simultaneous LLE and CE. The experimental data allow expanding the database on the phase and chemical equilibria in reacting systems and give the additional opportunities for the design of the process of ethyl propionate synthesis.

2. Experimental

2.1. Materials

Propionic acid (>0.98 mol fraction, BASF, Germany), ethanol

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Table 1
The purities of the chemicals.

Substance	Purity, initial mole fraction	Purity, final mole fraction ^a
Propionic acid	0.980	0.990
Ethanol	0.960	0.960 ^b
Ethyl propionate	0.980	0.997
Water	0.999	0.999

^a The uncertainty is estimated to be ± 0.002 mol fraction.

^b Ethanol sample contains 0.040 mol fraction of water.

(>0.96 mol fraction, Vekton, Russia) and ethyl propionate (>0.98 mol fraction, Vekton, Russia) were purified by distillation, water was bidistilled. Purity was determined by gas chromatography (GC) and is given in Table 1. All physical–chemical constants of pure substances are in agreement with the NIST data [5]. The fact that water is one of the components of the system under the study, gives the ability to use ethanol containing a known amount of water instead of absolute alcohol: this facilitated the experimental procedure. The amount of water remaining in ethanol after distillation was taken into account in preparation of initial mixtures.

2.2. CE determination

The study of the CE at 303.15 and 313.15 K was carried out using ¹H NMR spectroscopy (for homogeneous solutions) and GC analysis (for heterogeneous area) by methods describing in Refs. [6,7].

Initial quaternary mixtures of known overall compositions were prepared by gravimetric method in NMR-tubes (178 mm \times 4.2 mm i.d.) using an analytical balance Shinko VIBRA HT-120CE (Japan) with the accuracy of 0.001 g. Hydrochloric acid was used as a catalyst in amount of 0.003 mol fraction. NMR-tubes were placed in the liquid thermostat (303.15 and 313.15 K). The temperature uncertainty was ± 0.05 K. The CE was reached in no longer than 4 days (303.15 and 313.15 K). All samples were analyzed using a 500 MHz Bruker AVANCE III NMR spectrometer, equipped with a BBI probe head with inner coil for ¹H nuclei. The spectra were acquired with an acquisition time of 3 s, a relaxation delay of 1 s, and a pulse with 30° flip angle. The 16 scans were accumulated. The spin–lattice NMR relaxation times T_1 for all molecular groups of all compounds were measured. Observed T_1 values are in range from 3 to 5 s. The relaxation delay was high enough for quantitative analysis of peak integrals since the relaxation times had close values and the flip angle of pulse was relatively small. The error introduced by saturation was below 1%. The processing of the acquired spectra was carried out using Bruker TopSpin software. The phase correction was done manually. Polynomial baseline correction was done automatically. The integration region of 250–500 Hz which was over 20 times wider than the linewidth of analyzed peak was chosen. The constancy of composition confirmed the achievement of CE. The uncertainty of the determination of the peak areas introduced by the processing is estimated to be 3%.

In the case of the splitting of chemically equilibrium mixtures the compositions were determined using GC analysis. Gas chromatograph “Chromatec Crystal 5000.2” (Russia) with thermal conductivity detector (TCD) and packed column Porapak R

(1 m \times 3 mm i.d.) was used. The TCD was chosen because of the presence of water. Helium with the flow rate of 60 ml/min was used as a carrier gas. Operating temperature of column, vaporizing injector and TCD were 483 K, 503.15 K and 513 K, respectively. Initial quaternary mixtures were prepared by gravimetric method in glass vessels (5 ml) using an analytical balance Shinko VIBRA HT-120CE (Japan) with the accuracy of 0.001 g. The CE was reached in no longer than 4 days (303.15 and 313.15 K). After reaching of CE and phase equilibrium heterogeneous samples were taken from both phases with chromatographic syringe (“Hamilton”, USA) and analyzed by GC. To avoid the splitting of samples directly into the needle the chromatographic syringe was preliminary heated. The methods of internal standard and relative calibration were used to determine the compositions of CE. Propionic acid was accepted as linking component. Uncertainty of GC analysis averaged ± 0.005 mol fraction. Accuracy of initial solutions preparing was 0.001 g. The temperature uncertainty of the liquid thermostat was ± 0.05 K. The reproducibility of the experimental data was confirmed by the repeated analysis of samples. All chemically equilibrium mixtures were analyzed 3–5 times and the deviations of the results were in the frame of GC analysis uncertainties.

To check the consistency between two analytical methods (GC and NMR), we also determined few compositions in homogeneous area by GC analysis. The discrepancy does not exceed 0.005 mol fractions. In general both of methods enable to accurately determine the compositions of mixtures, but NMR method takes less time in comparison with GC analysis [6].

3. Results and discussions

3.1. Experimental data

The data on CE in homogeneous area of composition in propionic acid + ethanol + ethyl propionate + water system at 303.15 and 313.15 K and atmospheric pressure (NMR method) are presented in Table 2.

The data of Table 2 gives the opportunity to calculate the values of so-called concentration constants (pseudoreaction equilibrium constants)

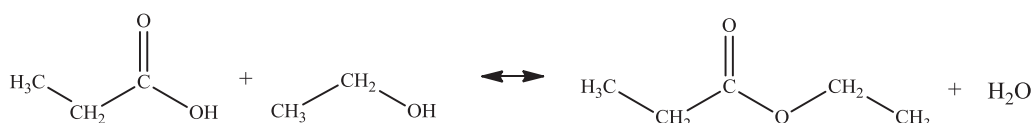
$$K_x = \frac{x_{\text{ethyl propionate}} x_{\text{water}}}{x_{\text{propionic acid}} x_{\text{ethanol}}}$$

which depends on the composition and should be not considered as real thermodynamic constant of CE. On the other hand the relative constancy of K_x can be used to check the consistency of the data. The average K_x values for homogeneous area of CE are 5.5 ± 1.0 at 303.15 K and 5.0 ± 0.9 at 313.15 K.

The consistency of the CE data is also confirmed by the fact that in all cases the initial and final (CE) compositions belong to the same stoichiometric line (within standard uncertainties $u(x)$).

The data on CE and LLE for the heterogeneous region at 303.15 and 313.15 K and atmospheric pressure (GC analysis) are presented in Table 3.

The compositions of chemically equilibrium mixtures in the case of ester synthesis reaction



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